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GAS CHROMATOGRAPHIC DETERMINATION OF THE PRODUCTS OF
DESTRUCTION OF POLYMER MATERIALS
BY RADIATION STERILIZATION

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At the present time, ionizing beta and gamma radiation (average dose level 2.5 Mrad) is used for sterilizing polymer materials for medical purposes, in addition to heat treatment. Although the degree of the destructive changes caused by irradiation of polymer materials and parts made of them at these doses is low, the products which are liberated in this process of destruction are capable of being absorbed on the surfaces of medical equipment, which is undesirable if the latter are to be used for medical purposes. The study of decomposition of the products of destruction may yield valuable information on the processes which take place in polymer materials during sterilization.

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The present paper is devoted to a study of the method of determining the gaseous products of radiation destruction, formed in the process of sterilization. We know from the data in the literature [1-3] that the principal gaseous products of radiation destruction of polymers are hydrogen, carbon monoxide and

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dioxide, oxygen and hydrocarbons from C_1 to C_5 . The identification of these components poses considerable difficulty. The mass spectrometric methods currently used for this purpose are tedious, complex and not always capable of providing an unambiguous idea of the qualitative composition of the complex gas mixture under study. The quantitative determination of trace impurities also poses a quite complex experimental problem.

The use of gas chromatography, which lacks these shortcomings and has a number of advantages, expands the possibilities open to us in studying decomposition of destruction products. In this work, we used the "TSVET-4" chromatograph with two detectors (katharometer and flame-ionization type) for simultaneous determination of hydrogen, carbon monoxide and dioxide, oxygen and hydro- | carbon from methane to pentane; the device was equipped with a supplementary recording potentiometer. In order to separate the hydrogen, carbon monoxide and dioxide, oxygen and nitrogen, | we used a system of chromatographic columns with SKT activated charcoal (fraction 0.25 - 0.5 millimeters, column length 3 meters) and with molecular screens, SA Kh) (the same fraction, column length 2 meters). The activated charcoal was first heated in a stream of nitrogen to 350 degrees for five hours. The molecular screens were heated to 350 degrees for 4 hours, then heated in a stream of nitrogen at 100 degrees for another four hours.

To separate the $C_1 - C_5$ hydrocarbons, we used a column 9.4 meters long with an internal diameter of 3 mm, composed of three sections. The first section | was 20% beta, beta 1-oxydipropionitrile on a TZK carrier, 6 meters long; the second was 20% polyethylene glycol (molecular wt. 1500) on TZK, 3 meters long, and the third was aluminum oxide, 0.4 meters long. The TZK fraction from 0.25 to 0.5 mm was used. The column containing aluminum oxide was used to improve the separation of the ethane and ethylene, propane and propylene. The aluminum oxide was first heated in a muffle furnace at 500 degrees for four hours.

Both systems of columns were placed in a thermostat at 40 degrees. The carrier gas was helium. The velocity of the carrier gas in the first system of columns was 70 ml/min, in the second system of columns 50 ml/min. The maximum pressure at the inlet of the columns was 1.8 at.

For a simultaneous determination of hydrogen, oxygen, nitrogen, carbon monoxide and dioxide at 40 degrees (taking into account the irreversible adsorption of carbon dioxide on the zeolite), the columns containing the activated charcoal and molecular screens were connected in series to one of the chambers of the katharometer (Figure 1). Figure 2a shows the chromatogram of a model mixture of hydrogen, oxygen, nitrogen, methane, carbon monoxide and carbon dioxide. The chromatogram shows repeated peaks of all components, extending in various directions due to the above mentioned connection of the columns. The absence of a carbon monoxide peak on the chromatogram following the column with activated charcoal (upper part of the chromatogram) is explained by the coincidence of the time of emergence of the carbon monoxide with the time of the change in sensitivity. The time of change in sensitivity of the detector in the chromatogram is indicated by arrows. The sensitivity of determination of carbon monoxide and dioxide is 10^{-3} mg. The chromatogram of the C_1-C_5 mixture is shown in Figure 2b. The threshold of sensitivity of hydrocarbon determination is approximately 5×10^{-6} mg for butane. Identification of the peaks in the chromatogram was performed both by direct introduction of individual components into the column and on the basis of the relative dwell times following preliminary calibration.

This method was used for determining the composition of gaseous products formed during the irradiation of certain polymer materials at small doses. Figure 3 shows the chromatograms of a

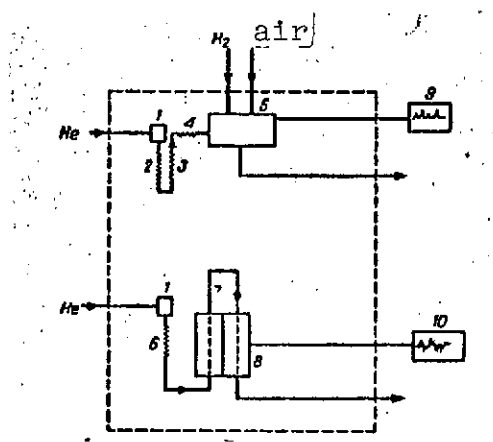


Figure 1. Diagram of chromatograph for analyzing products of polymer destruction.

1- device for introducing samples; 2- chromatographic column with 20% beta, beta' oxydipropionitrile on TZK; 3- column with 20% polyethylene glycol (molecular weight 1500) on TZK; 4- column containing aluminum oxide; 5- flame-ionization detectors; 6- column with SKT activated charcoal; 7- column with molecular screens, SA Kh; 8- katharometer; 9, 10- recording potentiometers; 11- thermostat

mixture of hydrocarbons formed following irradiation of samples of low-pressure polyethylene in a cobalt apparatus at a total dose of 2.5-3 Mrad. The samples of material were sealed in glass ampoules, both in a vacuum (Figure 3b) and in the presence of air (Figure 3a). We can see from Figure 3 that when the polyethylene was irradiated with a sterilizing dose the composition of the gas phase was quite complex. The presence of oxygen in the air had a significant influence upon the chromatographic spectrum of the products of radiation destruction. The products of radiolysis included various hydrocarbons; methane, ethane, propane, isobutane, n-butane, trans-butene-2 and isopentane. When polyethylene was irradiated in air, the concentration of trans-butene-2 in the gas phase was higher than in the case of irradiation in a vacuum. In addition, the products of radiation destruction of polyethylene irradiated in the presence of oxygen included hydrogen, carbon

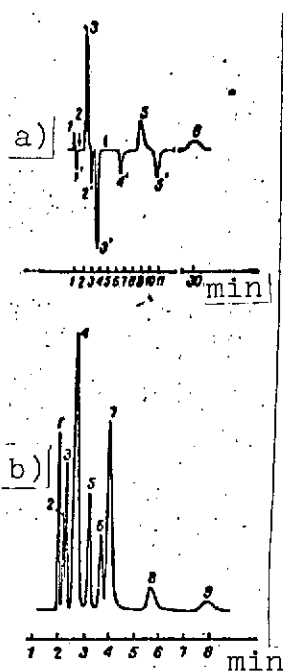


Figure 2. Chromatograms of model mixtures.

a: 1,1' - hydrogen; 2,2' - oxygen; 3,3' - nitrogen; 4- carbon monoxide, 5,5' - methane; 6 - carbon dioxide (detector katharometer); b: 1- methane; 2- ethane; 3- ethylene; 4- propane; 5- propylene; 6- isobutane; 7- n-butane; 8- butylene; 9- pentane (flame-ionization detector).

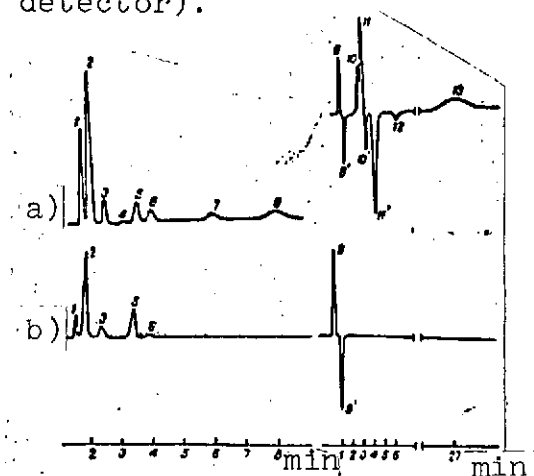


Figure 3. Chromatograms of a mixture of hydrocarbons formed as a result of radiation destruction of polyethylene (low pressure), irradiated in a cobalt apparatus with a dose of 2.5 Mrad.

a- in the presence of atmospheric oxygen; b- in vacuum: 1- methane; 2- ethane; 3- propane; 4- propylene; 5- isobutanes; 6- N-butanes; 7- transbutene-2; 8- N-pentane; 9,9'-hydrogen; 10,10'-oxygen; 11,11'-nitrogen; 12- carbon monoxide; 13- carbon dioxide.

monoxide and carbon dioxide in significant concentrations; the amount of carbon dioxide was about seven times greater than that of carbon monoxide. The products of destruction of polyethylene irradiated in a vacuum did not include carbon monoxide or carbon dioxide. It is likely that the presence of oxygen leads to significant oxidative processes during irradiation and to the formation of products containing oxygen.

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